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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Ian Anthony Jones and Roger Jeremy Wise

Serial No. : 09/806,613

Group : 1725

Filed : March 29, 2001

Examiner: M. Alexandra Elve

For : WELDING METHOD

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LETTER SUBMITTING FURTHER COPY OF DOCUMENT

Commissioner for Patents  
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Sir:

Martin Novack  
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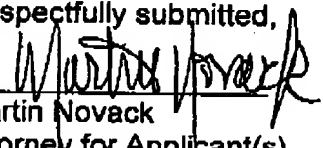
The Office Action dated October 15, 2004, indicates that the document "Iridion  
LS For The Laser Marking of Plastics", Merck Brochure, June, 1997, is not present in  
the file. The document was submitted as one of the 46 documents filed with a  
Supplemental Information Disclosure Statement and Form PTO-1449 that were  
received at the USPTO on March 4, 2004, as evidenced by a stamped  
acknowledgement postcard from the USPTO (copy attached). However, since the  
document is now apparently missing at the USPTO, Applicant submits a further copy

herewith. [For the Examiner's convenience, an informal copy is also being faxed to the Examiner.] It is respectfully requested that the subject document should now be made "of record."

Delray Beach, Florida  
Tel. (561) 498-4706  
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October 20, 2004

(M-39)

Respectfully submitted,

  
Martin Novack  
Attorney for Applicant(s)

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This acknowledges receipt at the PTO, on the  
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SUPPLEMENTAL INFORMATION  
DISCLOSURE STATEMENT (3 sheets);  
FORM PTO-1449 (3 sheets); 48 DOCUMENT  
COPIES AND 10 TRANSLATIONS  
in the following application:  
Applicants: Ian Anthony Jones et al  
Serial No.: 09/806,613  
Filed : March 29, 2001  
For : WELDING METHOD  
Docket No.: GJE-5825

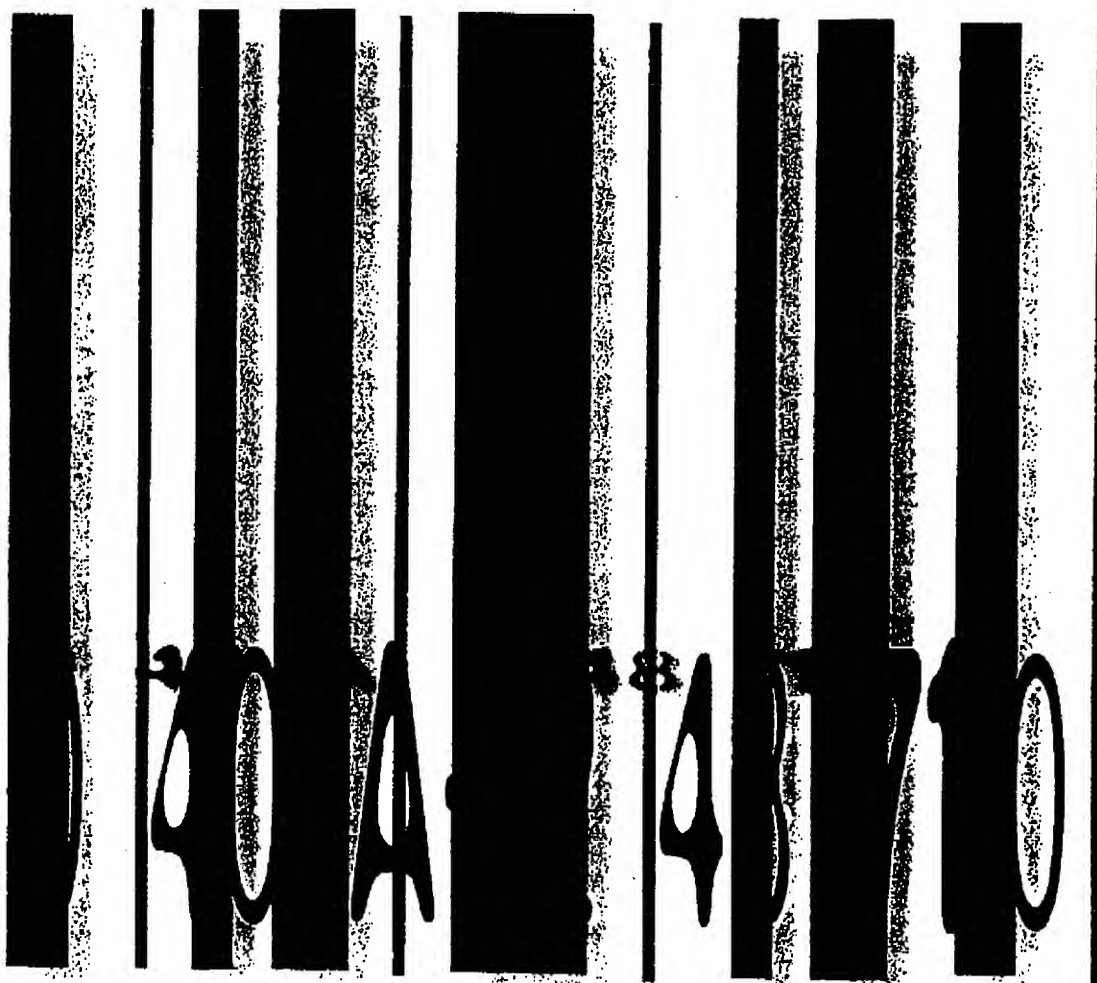


m31

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# Iriodin<sup>®</sup> LS

## for the laser marking of plastics



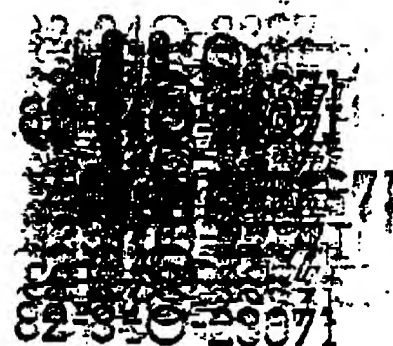
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## Introduction

Today, the marking of manufactured goods has become a standard feature of almost every production process. Hot embossing, printing, punching and engraving are the most commonly used methods of transferring lettering, symbols or decorative features onto the surface of manufactured goods.

The requirements placed on the quality of the appearance of the marking, the marking speed, the environmental compatibility of the method used and its flexibility are continually increasing. At the same time, marking costs should remain as low as possible. These demands are met by a technology which, in recent years, is becoming more and more important in the market:



### The marking, coding and lettering with laser beams

The abrasion of printing ink with lasers is the most common application of this technology. The marking is made by the contrast of the printed ink onto the different coloured background. To date, this form of laser labelling has become completely established in many application areas - for example in the beverages industry.

This method does not adequately use a further important advantage of laser marking technology. This is the possibility of making the mark permanent and impossible to forge. For this, the marking must be made directly on or inside the surface of the object to be marked.

In metals, the marking is carried out by laser with a relatively simple engraving on the surface. Markings made in this way are generally more prominent than those made with previous technologies such as mechanical engraving, etching, etc. However, these laser markings are still a long way off from the intensity of a print.

A quality which is comparable with that of a print is often required in the marking of plastics, particularly in the packaging field. Until recently, it was only possible to obtain such a laser marking easily in a few plastics (e.g. PVC). The majority of plastics, e.g. polyolefins, could not be marked by laser or only with inadequate results.

## Lasermarking of plastics

The development of laser-markable plastics is a challenge to many companies and indeed, there are special, laser-markable plastic types available on the market. These materials, however, are designed for certain applications and do not offer the large variety of different applications which standart plastics do. In addition they are only available in a few colors. In contrast, completely new perspectives for the laser marking of plastics are opened up if standard plastics, in any colour whatsoever, can be made laser markable.

In this respect, Merck has made a considerable step forward. In close co-operation with laser instrument manufacturers, the continuous development and optimisation of the Iriodin® pigment range have now made the laser marking of many plastics, no matter what colour, possible. Where up to now only insignificant markings were possible, today, clearly contrasted markings are available. For this, Merck has developed a separate product range: the Iriodin® LS types (LS = laser sensitive).

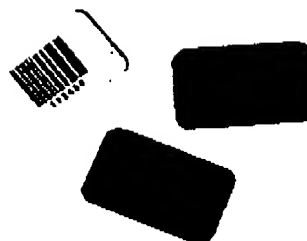
### Why can only poorly contrasted markings be made on standard plastics using a laser beam?

Generally, mechanisms which do not cause a strong colour reaction will only produce poorly contrasted lettering which do not even fulfill the minimum legibility requirements.

The main reasons for this are:

#### \* Transparency of the plastic

The absorption of the plastic is too low for the laser light. Therefore, the laser light goes straight through the plastic without making any substantial changes. A marking is possible after repeated bombardment or at very high laser beam intensities. The stress caused to the material, however, is so high that deep-reaching destruction of the polymer takes place and the marking is still insufficiently clear. The mass production plastics polyethylene, polypropylene and polystyrene are such materials.



Lasermarked bar codes on PE  
with Iriodin® LS 800

**Poor contrasting of the marking**

Engraving: There is enough absorption present, but the plastic spontaneously depolymerises under the load. In most plastics, the resulting engraving is too poorly contrasted to serve as an easily legible marking.

**Formation of cracks and bubbling**

If the laser action leads to the formation of fine cracks or bubbling on the surface, this can indeed lead to a well-contrasted, whitish marking in dark coloured plastics.

**Dullness as a result of surface changes caused by melting**

Such markings are only visible from certain angles of observation. The contrast is not sufficient for good legibility.

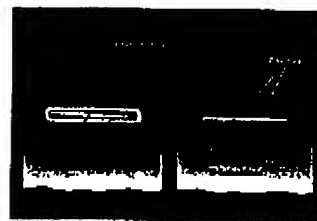
**Marking of plastics with contrasting colour reactions**

As a general rule, contrasting colour reactions can be provided by chemical reactions in the additives (e.g. colour changes of pigments) or in the polymer matrix (dark colouring due to carbonisation). The important factor in such reactions is that the colours are bright enough and that they are irreversible.

The addition of Iriodin®/Iriodin® LS pigments permits intensive dark or light markings in many plastics under laser treatment. These are caused by a reaction of the polymer and partly also by a reaction in the pigment itself.

Depending on the type of plastic, the pigment and the laser, these markings range from white to black. They are irreversible and avoid an unnecessarily heavy destruction of the polymer because they occur at a relatively low laser intensity in areas near to the surface of the material.

Iriodin®/Iriodin® LS Pigments thus offer the ideal solution for the marking of plastics with laser beams:



*Reaction mechanism with Iriodin® pigments hit by a laser beam in plastics*



*Lasermarked PE with Iriodin® LS 800*



## Product range

### Iriodin® pearl lustre pigments

In the 80's Merck found out that the incorporation of pearlescent pigments, based on mica /TiO<sub>2</sub>, in many of the standard plastics make these polymers receptive to the light of a CO<sub>2</sub> laser and a visible mark with good contrast was achievable at a relatively low laser intensity. Iriodin pearl lustre pigments are available in the shining colours silver (100 series), interference (200 series), gold (300 series) as well as copper and bronze (500 series). Pearlescent pigments are commonly known for their decorative enhancement to plastic products and their sensitivity to laser light could now be used as an additional functional capacity.

When laser marking a product is a requirement, but the pearlescent appearance is not necessary or desired, it is possible to cover up the pearl effect with opaque pigments, for example TiO<sub>2</sub>, without any negative effect on the lasermarking results.

However a higher loading of opaque pigments has a strong influence on colours and is therefore not recommended for coloured or natural plastics.

For that reason Merck has developed a separate product range particularly designed for the laser marking technology:

The Iriodin® LS pigments (LS-laser sensitive).

The Iriodin® LS pigments offer a lot of advantages in comparison to pearl pigments or special lasermarkable plastics.

Iriodin® LS pigments make possible

- the laser marking of standard plastics
- well-contrasted markings at low laser intensities
- an economic marking due to low pigment concentrations

Iriodin® LS pigments are

- simple to mix into the plastic material in several different ways
- can be easily incorporated in existing formulations
- have no important influence on the properties of the material

The following products are available for all laser types which are actually in use for lasermarking plastics:

		Particle size*	Colour	Recommended laser type
Art.no 6825	Iriodin® LS 800	> 15 µm	transparent	CO <sub>2</sub> Laser
Art.no 4781	Iriodin® LS 805	2-100 µm	transparent	CO <sub>2</sub> Laser
Art.no 4784	Iriodin® LS 810	2-28 µm	white	CO <sub>2</sub> Laser
Art.no 4782	Iriodin® LS 820	< 15 µm	light grey	Nd: YAG
Art.no 4783	Iriodin® LS 825	< 15 µm	transparent- blue grey	Nd: YAG
Art.no 4779	Iriodin® LS 830	10-60 µm	black	all laser types
Art.no 4786	Iriodin® LS 835	< 15 µm	black	all laser types
Art.no 4785	Iriodin® LS 850	< 15 µm	blue	all laser types

\* Iriodin® pigments are thin platelets. The above particle sizes refer to platelet diameter.



Lasermarked HDPE bottle with Iriodin®

## Marking results

The marking results which are obtainable depend on the following factors:

- plastic type
- type of laser
- Iriodin®/ Iriodin® LS type

The most suitable Iriodin®/Iriodin® LS type and the optimum pigment concentration must be determined. The presence of other additives in the formulation, such as colorants and fillers, can affect the marking results although the plastics remain markable in most cases (exception: carbon black at > 0.2 %, as explained later under black plastics).



Lasermarked  
HDPE bottle  
with Iriodin®

## Marking results Polyethylene

### CO<sub>2</sub> - mark laser

#### • Natural material

**Recommended Iriodin® LS type:**

Iriodin® LS 800 or Iriodin® LS 805

**Recommended concentration:**

0,1 - 0,3 % to the existing formulation  
dark

**Colour of the marking:**

**General aspects:**

Iriodin LS 800 as well Iriodin LS 805 are totally transparent.  
Therefore the addition show no negative influence on the original colour.

#### • White material

**Recommended Iriodin® LS type:**

Iriodin® LS 810

**Recommended concentration:**

0,1 - 0,5 % to the existing formulation  
dark

**Colour of the marking:**

**General aspects:**

Iriodin® LS 810 is a whitish transparent pigment which shows an improved marking behavior in comparison to Iriodin® LS 800 or Iriodin® LS 805. Especially in low density polyethylene Iriodin® LS 800 offers an ideal way to achieve dark markings of high contrast.

#### • Coloured material

**Recommended Iriodin® LS type:**

Iriodin® LS 800 / Iriodin® LS 805 or Iriodin® LS 810

**Recommended concentration:**

0,1 - 1 % to the existing formulation

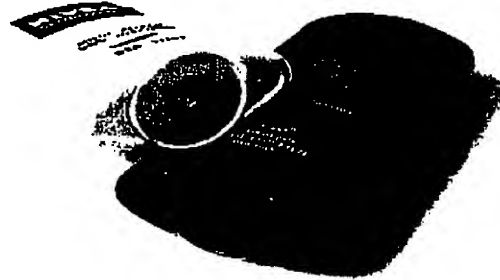
**Colour of the marking:**

depending on the concentration dark or whitish

**General aspects:**

Due to the transparency of Iriodin® LS 800 and Iriodin LS 805 they are suitable to be added to existing formulations without changing the original colour of the formulation. By adding concentrations up to 0,3 % the markings are dark. The further addition up to 1 % lead to markings which are more and more whitish. Those markings are of high contrast, especially on dark formulations. Iriodin LS 810 can be used to replace small amounts of TiO<sub>2</sub> of the original formulation to achieve dark markings in e.g. low density polyethylene.

LDPE deo sticks with  
Iriodin® LS marked by a  
CO<sub>2</sub> mask laser.



#### Black material

**Recommended Iriodin® LS type:**

**Recommended concentration:**

**Colour of the marking:**

**General aspects:**

Iriodin® LS 830 or LS 835

0,2 - 1 % depending to the hiding power requested  
whitish

To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior.

ALL TEST TEST  
LASER MARKING TECHNOLOGY  
0123456789



#### Not YAG laser

##### Natural, white and coloured material

**Recommended Iriodin® LS type:**

**Recommended concentration:**

**Colour of the marking:**

**General aspects:**

Iriodin® LS 820 or Iriodin® LS 825

0,1 - 0,3 % to the existing formulation

dark

Iriodin® LS 820 as well Iriodin® LS 825 show a very low colour impact.  
Therefore the addition show nearly no influence on the original colour.

##### Black material

**Recommended Iriodin® LS type:**

**Recommended concentration:**

**Colour of the marking:**

**General aspects:**

Iriodin® LS 830 or LS 835

0,2 - 1 % depending to the hiding power requested

whitish

To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior.

Lasermarked PE with  
Iriodin® LS 810 (white) and  
Iriodin® LS 850 (dark blue)

## Marking results Polypropylene

#### CO<sub>2</sub> - mask laser

##### Natural material

**Recommended Iriodin® LS type:**

**Recommended concentration:**

**Colour of the marking:**

Iriodin® LS 800 / Iriodin® LS 805 or LS 810

0,1 - 0,3 % to the existing formulation

whitish or dark

**General aspects:**

Iriodin® LS 800 as well Iriodin® LS 805 are totally transparent. Therefore the addition show no negative influence on the original colour. The markings are whitish with a good contrast. For dark markings Iriodin® LS 810 should be used, however there is a certain influence on the transparency.

**White material**

**Recommended Iriodin® LS type:**

Iriodin® LS 810

**Recommended concentration:**

0,1 - 0,5 % to the existing formulation

**Colour of the marking:**

dark

**General aspects:**

Iriodin® LS 810 is a whitish transparent pigment which shows an improved marking behavior in comparison to Iriodin® LS 800 or Iriodin® LS 805.

*Lasermarked PP Lids with  
Iriodin® LS 830*

**Coloured material**

**Recommended Iriodin® LS type:**

Iriodin® LS 800 / Iriodin® LS 805 or Iriodin® LS 810

**Recommended concentration:**

0,1 - 1 % to the existing formulation

**Colour of the marking:**

depending on the concentration dark or whitish

**General aspects:**

Due to the transparency of Iriodin® LS 800 and Iriodin® LS 805 they are suitable to be added to existing formulations without changing the original colour of the formulation. By adding concentrations up to 0,3 % the markings are whitish. Those markings are of high contrast, especially on dark formulations. Iriodin® LS 810 can be used to replace small amounts of TiO<sub>2</sub> of the original formulation to achieve dark markings.

**Black material**

**Recommended Iriodin® LS type:**

Iriodin® LS 830 or LS 835

**Recommended concentration:**

0,2 - 1 % depending to the hiding power requested

**Colour of the marking:**

whitish

**General aspects:**

To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior.

**Nd: YAG laser****Natural, white and coloured material**

**Recommended Iriodin® LS type:**

Iriodin® LS 820 or Iriodin® LS 825

**Recommended concentration:**

0,1 - 0,3 % to the existing formulation

**Colour of the marking:**

dark

**General aspects:**

Iriodin® LS 820 as well Iriodin® LS 825 show a very low colour impact. Therefore the addition show nearly no influence on the original colour.

Black material  
*Recommended Iriodin® LS type:*  
*Recommended concentration:*  
*Colour of the marking:*  
*General aspects:*

Iriodin® LS 830 or LS 835  
 0,2 - 1 % depending to the hiding power requested  
 whitish  
 To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior.

## Marking results Polystyrene

### CO<sub>2</sub> - mask laser

#### Natural material

*Recommended Iriodin® LS type:*  
*Recommended concentration:*  
*Colour of the marking:*  
*General aspects:*

Iriodin® LS 800 or Iriodin® LS 805  
 0,1 - 0,3 % to the existing formulation  
 white  
 Iriodin® LS 800 as well Iriodin® LS 805 are totally transparent. Therefore the addition show no negative influence on the original colour.

#### White material

*Recommended Iriodin® LS type:*  
*Recommended concentration:*  
*Colour of the marking:*  
*General aspects:*

Iriodin® LS 810  
 0,1 - 0,5 % to the existing formulation  
 grey  
 Iriodin® LS 810 is a whitish transparent pigment which shows an improved marking behavior in comparison to Iriodin® LS 800 or Iriodin® LS 805.

#### Coloured material

*Recommended Iriodin® LS type:*  
*Recommended concentration:*  
*Colour of the marking:*  
*General aspects:*

Iriodin® LS 800 / Iriodin® LS 805 or Iriodin® LS 810  
 0,1 - 1 % to the existing formulation  
 depending on the concentration dark or whitish  
 Due to the transparency of Iriodin® LS 800 and Iriodin® LS 805 they are suitable to be added to existing formulations without changing the original colour of the formulation. By adding concentrations up to 0,3 % the markings are dark. The further addition up to 1 % lead to markings which are more and more whitish. Those markings are of high contrast, especially on dark formulations. Iriodin® LS 810 can be used to replace small amounts of TiO<sub>2</sub> of the original formulation to achieve dark markings.

#### Black material

*Recommended Iriodin® LS type:*  
*Recommended concentration:*  
*Colour of the marking:*  
*General aspects:*

Iriodin® LS 830 or LS 835  
 0,2 - 1 % depending to the hiding power requested  
 whitish  
 To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior.

**Nd: YAG laser**

- Natural, white and coloured material

**Recommended Iriodin® LS type:** Iriodin® LS 820 or Iriodin® LS 825  
**Recommended concentration:** 0,1 - 0,3 % to the existing formulation  
**Colour of the marking:** dark  
**General aspects:** Iriodin® LS 820 as well Iriodin® LS 825 show a very low colour impact. Therefore the addition show nearly no influence on the original colour. Polystyrene in general marks well with the Nd:YAG laser. The addition of Iriodin® LS 820 or Iriodin® LS 825 increase the sensibility of the material. The advantages are higher marking speed, better definition of the markings, better surface quality of the marking as well as lower laser energy needed.

- Black material

**Recommended Iriodin® LS type:** Iriodin® LS 830 or LS 835  
**Recommended concentration:** 0,2 - 1 % depending to the hiding power requested  
**Colour of the marking:** whitish  
**General aspects:** To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior. Due to the fact that polystyrene marks black in general two marking mechanisms take place at the same time. A dark marking from the material itself, as well as a whitish marking caused by Iriodin® LS 830 or Iriodin® LS 835.

## Marking results in PET

**CO<sub>2</sub> - mask laser**

- Natural material

**Recommended Iriodin® LS type:** Iriodin® LS 800 or Iriodin® LS 805  
**Recommended concentration:** 0,1 - 0,3 % to the existing formulation  
**Colour of the marking:** white  
**General aspects:** Iriodin® LS 800 as well Iriodin® LS 805 are totally transparent. Therefore the addition show no negative influence on the original colour.

- White material

**Recommended Iriodin® LS type:** Iriodin® LS 800 or LS 805  
**Recommended concentration:** 0,1 - 0,3 % to the existing formulation  
**Colour of the marking:** white  
**General aspects:** Unfortunately it is not possible to achieve dark markings on white PET.



Lasermarked PET plastic plates  
 with Iriodin® LS 800 (right)  
 and without (left)

**\* Coloured material****Recommended Iriodin® LS type:**

Iriodin® LS 800 or Iriodin® LS 805

**Recommended concentration:**

0,1 - 3 % to the existing formulation

**Colour of the marking:**

white

**General aspects:**

Due to the transparency of Iriodin® LS 800 and Iriodin® LS 805 they are suitable to be added to existing formulations without changing the original colour of the formulation. By adding concentrations up to 0,3 % the markings are white and show good contrast on coloured materials.

**\* Black material****Recommended Iriodin® LS type:**

Iriodin® LS 830 or LS 835

**Recommended concentration:**

0,2 - 1 % depending to the hiding power requested

**Colour of the marking:**

whitish

**General aspects:**

To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior.

**Nd: YAG laser****\* Natural, white and coloured material****Recommended Iriodin® LS type:**

Iriodin® LS 820 or Iriodin® LS 825

**Recommended concentration:**

0,1 - 0,3 % to the existing formulation

**Colour of the marking:**

dark

**General aspects:**

Iriodin® LS 820 as well Iriodin® LS 825 show a very low colour impact. Therefore the addition show nearly no influence on the original colour PET in general marks well with the Nd:YAG laser. The addition of Iriodin® LS 820 or Iriodin® LS 825 increase the sensibility of the material. The advantages are higher marking speed, better definition of the markings, better surface quality of the marking as well as lower laser energy needed.

**\* Black material****Recommended Iriodin® LS type:**

Iriodin® LS 830 or LS 835

**Recommended concentration:**

0,2 - 1 % depending to the hiding power requested

**Colour of the marking:**

whitish

**General aspects:**

To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior. Due to the fact that polystyrene marks black in general two marking mechanisms take place at the same time. A dark marking from the material itself, as well as a whitish marking caused by Iriodin® LS 830 or Iriodin® LS 835.

## Marking results Polycarbonate

### CO<sub>2</sub> - mask laser

#### Natural material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 800 or Iriodin® LS 805

0,1 - 0,5 % to the existing formulation

dark

Iriodin® LS 800 as well Iriodin® LS 805 are totally transparent. Therefore the addition show no negative influence on the original colour.

#### White material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 810

0,1 - 0,5 % to the existing formulation

dark

Iriodin® LS 810 is a whitish transparent pigment which shows an improved marking behavior in comparison to Iriodin® LS 800 or Iriodin® LS 805.

#### Coloured material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 800 or Iriodin® LS 805

0,1 - 3 % to the existing formulation

dark

Due to the transparency of Iriodin® LS 800 and Iriodin® LS 805 they are suitable to be added to existing formulations without changing the original colour of the formulation. By adding concentrations up to 0,3 % the markings show dark markings on coloured materials.

#### Black material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 830 or LS 835

0,2 - 1 % depending to the hiding power requested

whitish

To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior.

### Nd: YAG laser

#### Natural, white and coloured material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 820 or Iriodin® LS 825

0,1 - 0,3 % to the existing formulation

dark

Iriodin® LS 820 as well Iriodin® LS 825 show a very low colour impact. Therefore the addition show nearly no influence on the original colour. Polycarbonate in general marks well with the Nd:YAG laser. The addition of Iriodin® LS 820 or Iriodin® LS 825 increase the sensibility of the material. The advantages are higher marking speed, better definition of the markings, better surface quality of the marking as well as lower laser energy needed.



**Black material****Recommended Iriodin® LS type:****Recommended concentration:****Colour of the marking:****General aspects:****Iriodin® LS 830 or LS 835**0,2 - 1 % depending to the hiding power requested  
whitish

To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior. Due to the fact that polycarbonate marks black in general two marking mechanisms take place at the same time. A dark marking from the material itself, as well as a whitish marking caused by Iriodin® LS 830 or Iriodin® LS 835.



Lasermarked PUR cattle  
tags with Iriodin® LS 820

## Marking results ABS

**CO<sub>2</sub> - mask laser****n Natural material****Recommended Iriodin® LS type:****Recommended concentration:****Colour of the marking:****General aspects:****Iriodin® LS 800 or Iriodin® LS 805**0,1 - 0,5 % to the existing formulation  
dark

Iriodin® LS 800 as well Iriodin® LS 805 are totally transparent.  
Therefore the addition show no negative influence on the original colour.

**z White material****Recommended Iriodin® LS type:****Recommended concentration:****Colour of the marking:****General aspects:****Iriodin® LS 810**0,1 - 0,5 % to the existing formulation  
dark

Iriodin® LS 810 is a whitish transparent pigment which shows an improved marking behavior in comparison to Iriodin® LS 800 or Iriodin® LS 805.

**a Coloured material****Recommended Iriodin® LS type:****Recommended concentration:****Colour of the marking:****General aspects:****Iriodin® LS 800 or Iriodin® LS 805**0,1 - 0,3 % to the existing formulation  
dark

Due to the transparency of Iriodin® LS 800 and Iriodin® LS 805 they are suitable to be added to existing formulations without changing the original colour of the formulation. By adding concentrations up to 0,3 % the markings show dark markings on coloured materials.

**Black material**  
**Recommended Iriodin® LS type:**  
**Recommended concentration:**  
**Colour of the marking:**  
**General aspects:**

Iriodin® LS 830 or LS 835  
 0,2 - 1 % depending to the hiding power requested  
 whitish  
 To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior.

#### **Nd: YAG laser**

**Natural, white and coloured material**

**Recommended Iriodin® LS type:**  
**Recommended concentration:**  
**Colour of the marking:**  
**General aspects:**

Iriodin® LS 820 or Iriodin® LS 825  
 0,1 - 0,3 % to the existing formulation  
 dark  
 Iriodin® LS 820 as well Iriodin® LS 825 show a very low colour impact. Therefore the addition show nearly no influence on the original colour. ABS in general marks well with the Nd:YAG laser. The addition of Iriodin® LS 820 or Iriodin® LS 825 increase the sensibility of the material. The advantages are higher marking speed, better definition of the markings, better surface quality of the marking as well as lower laser energy needed.

**Black material**

**Recommended Iriodin® LS type:**  
**Recommended concentration:**  
**Colour of the marking:**  
**General aspects:**

Iriodin® LS 830 or LS 835  
 0,2 - 1 % depending to the hiding power requested  
 whitish  
 To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior. Due to the fact that polycarbonate marks black in general two marking mechanisms take place at the same time. A dark marking from the material itself, as well as a whitish marking caused by Iriodin® LS 830 or Iriodin® LS 835.



Labeling of electronic  
 housings by Nd:YAG laser

## Marking results Polyamide

### CO<sub>2</sub> - mask laser

#### • Natural material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 800 or Iriodin® LS 805

0,1 - 0,5 % to the existing formulation

white

Iriodin® LS 800 as well Iriodin® LS 805 are totally transparent.

Therefore the addition show no negative influence on the original colour.

#### • White material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 800 or Iriodin® LS 805

0,1 - 0,3 % to the existing formulation

white

Unfortunately it is not possible to achieve dark markings on polyamide.

#### • Coloured material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 800 or Iriodin® LS 805

0,1 - 3 % to the existing formulation

white

Due to the transparency of Iriodin® LS 800 and Iriodin® LS 805 they are suitable to be added to existing formulations without changing the original colour of the formulation. By adding concentrations up to 0,3 % the markings show white markings on coloured materials.

#### • Black material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 830 or LS 835

0,2 - 1 % depending to the hiding power requested

whitish

To achieve whitish markings on a black material first tests should be done starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are black pigments which give the colour as well as the lasermarkability to the material. Combination with small amounts of black carbon (max. 0,1 %) are possible. Higher loadings of black carbon may have a negative influence on the marking behavior.

### Nd: YAG laser

#### • Natural, white and coloured material

*Recommended Iriodin® LS type:*

*Recommended concentration:*

*Colour of the marking:*

*General aspects:*

Iriodin® LS 820 or Iriodin® LS 825

0,1 - 0,3 % to the existing formulation

dark

Iriodin® LS 820 as well Iriodin® LS 825 show a very low colour impact.

Therefore the addition show nearly no influence on the original colour.



Labeling of  
electronic housings  
by Nd:YAG laser

**Coloured material****Recommended Iriodin® LS type:****Recommended concentration:****Colour of the marking:****General aspects:**

Iriodin® LS 820 or Iriodin® LS 825 and Iriodin® LS 800  
0,25 % (LS 825) and 0,8% Iriodin® LS 800 to the existing  
formulation

white

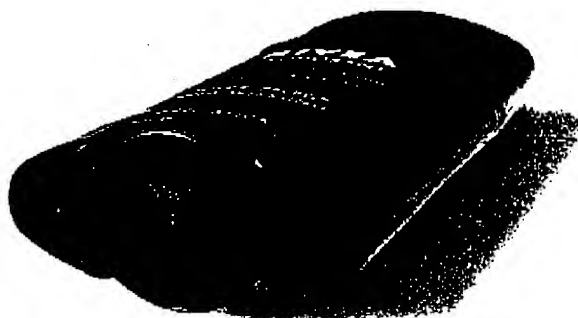
By using a combination of Iriodin® LS 820 or Iriodin® LS 825 together with  
Iriodin® LS 800 it is possible to achieve white markings with high contrast.  
In reinforced materials the concentration of the pigment should be increased.  
The relation should be approx. 1:4 (e.g. 0,4% Iriodin® LS 825 and 1,6%  
Iriodin® LS 800).

**Black material****Recommended Iriodin® LS type:****Recommended concentration:****Colour of the marking:****General aspects:**

Iriodin® LS 830 or LS 835

0,2 - 1 % depending to the hiding power requested  
whitish

To achieve whitish markings on a black material first tests should be done  
starting from a natural material. Iriodin® LS 830 and Iriodin® LS 835 are  
black pigments which give the colour as well as the lasermarkability to the  
material. Combination with small amounts of black carbon (max. 0,1 %) are  
possible. Higher loadings of black carbon may have a negative influence on  
the marking behavior. Due to the fact that polycarbonate marks black in  
general two marking mechanisms take place at the same time. A dark mar-  
king from the material itself, as well as a whitish marking caused by  
Iriodin® LS 830 or Iriodin® LS 835.



LDPE deo stick  
marked with CO<sub>2</sub> mark laser

## Properties of laser marking

The lettering, coding and marking of products with a laser beam in industrial production satisfies in every respect the highest demands. The advantages of laser marking are due to the special features of this technology:

Laser marking is carried out:

### without contact

- a high marking throughput without mechanical abrasion
- clean, sharply edged markings, also on soft, irregular or curved surfaces
- very small lettering in excellent quality

### inkless

- permanent, solvent-, wipe- and scratchproof markings
- no problems with combustible, volatile solvents and their disposal
- clean coding technology without expensive consumption materials

### at very high speed

- sharp edged marking on moving objects with exact positioning of the mark
- up to 6,000 markings a minute with a pulse TEA-CO<sub>2</sub> laser
- up to 2,000 mm/sec with an Nd:YAG laser

### very flexible, because

- can be programmed by software
- automatic mask changer
- very small lettering (0.5 mm character height) and line widths available
- very high resolution of the marking



PE bottle with Iriodin<sup>®</sup> marked by a DOT Matrix laser



Lasermarked PE plastics with Iriodin<sup>®</sup> LS 800

Character  
Size of mark  
(1) 100 µm (2)  
(2) 100 µm (3)  
(3) 100 µm (4)  
(4) 100 µm (5)  
(5) 100 µm (6)  
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(98) 100 µm (99)  
(99) 100 µm (100)



Lasermarked plastic label (Multi-layer polyolefins) with Iriodin<sup>®</sup>

**without previous treatment of the surface**

no adhesion problems, also when marking on polyethylene and polypropylene  
marking is made in and not on the plastic  
the presence of a wet coating on the surface has no negative effect on the marking

**very economic, because**

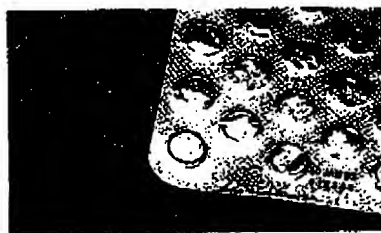
minimum servicing requirements  
no consumption materials  
fully automated coding  
the laser is quickly amortised

**impossible to forge**

permanent markings which cannot be removed without leaving clear signs of manipulation  
ideal for safety coding  
wipeproof due to the alteration of the material surface (penetration depth 20 - 200 µm)



*Lasermarked PE bottle with Iriodin® LS 810*



*Lasermarked transparent PP blister films with Iriodin® LS 800*

## Common methods in the laser marking of plastics

Depending on the type of material, the nature and purpose of the lettering and the marking speed, three different methods can be chosen

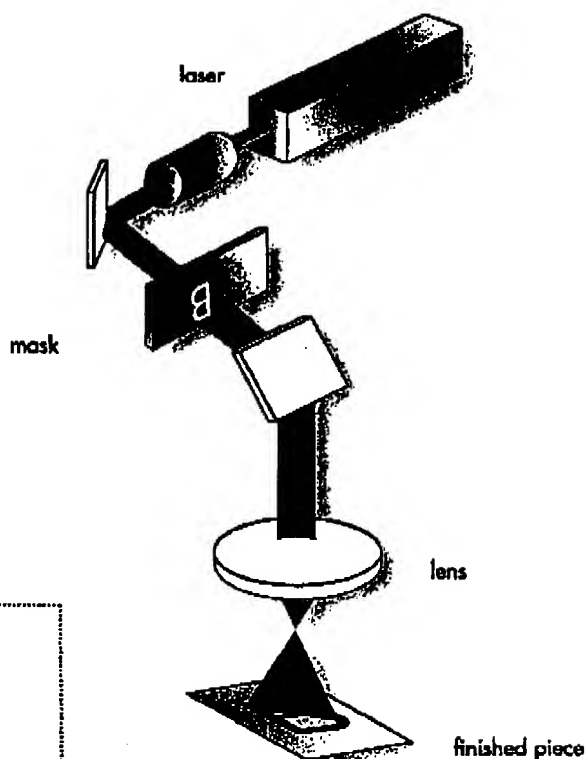
- masking method
- beam deflection method
- continuous beam method

The mask- and beam deflection methods are by far the most commonly applied technologies. The continuous beam method is only used in extreme cases, e.g., in marking metals, and can be discounted here.

### Mask method

In the masking method, the extremely short impulse of light energy is directed on the position to be marked. A metal mask in the path of the beam contains the letters, numbers or signs which are to be marked. The picture of the mask on the object is made using a lens. The energy density of the light rays (in  $J/cm^2$ ) is increased depending on the scale of the marking.

Schematic building of a mask system



These are:

pulsed TEA-CO<sub>2</sub> laser (wavelength 10,6 mm)

Excimer laser (wavelength 193 - 351 nm)

pulse Nd:YAG laser (wavelength 1064 nm)

Among the CO<sub>2</sub> lasers, the so-called dot-matrix lasers are a special case. The images they produce are similar to the print of an ink jet printer.

#### **Pulsed TEA-CO<sub>2</sub> laser**

(TEA = Transversal Excited Atmospheric Pressure)

Pulse TEA-CO<sub>2</sub> lasers, at a pulse length of only a few nanoseconds, cause carbonisation and therefore a change in the colour of the plastic surrounding the pigment. This carbonisation only takes place near the pigment particles at the surface of the object. The total stability of the material remains unchanged. In many cases, the pigment itself darkens. Plastics which have little tendency to carbonise undergo bubbling on the surface. Carbonisation and bubbling can take place simultaneously where the result is a light-grey marking.

Depending on the pigment concentration, the type of plastic used and the laser energy, carbonisation or bubbling can be created as required. The result is the choice of either light or dark marking. Experience has shown that low pigment concentrations (from 0.1 %) provide a dark marking and that higher concentrations (up to 1.5 %) show a light coloured marking. There is a gradual change from dark to light. Here though, the black colouring reaches a maximum. The optimum pigment concentrations to provide a well-contrasted marking at an economical price should be determined by experiment.

The following table shows the results of trials to establish the limit



Lasermarked HDPE-shampoo bottle with Iridium®



values for energy density which are required to mark various plastics. The gradation of energy density was 3.7 and 11 J/cm<sup>2</sup>. The individual plastics were pigmented with 0.5 % Iriodin® LS 810.

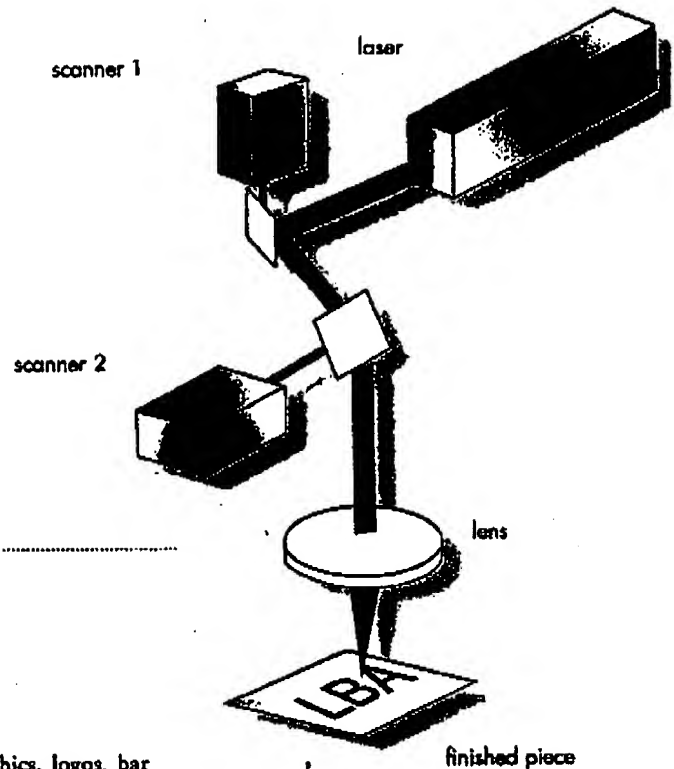
plastic	visible marking	easily legible marking
epoxy resin	7 J/cm <sup>2</sup>	—
PE	<3 J/cm <sup>2</sup>	3 J/cm <sup>2</sup>
PP	3 J/cm <sup>2</sup>	7 J/cm <sup>2</sup>
PS	<3 J/cm <sup>2</sup>	3 J/cm <sup>2</sup>
ABS	<3 J/cm <sup>2</sup>	3 J/cm <sup>2</sup>
PET	7 J/cm <sup>2</sup>	11 J/cm <sup>2</sup>
PVC	3 J/cm <sup>2</sup>	7 J/cm <sup>2</sup>
PC	<3 J/cm <sup>2</sup>	3 J/cm <sup>2</sup>

Without pigmenting, only PVC from about 7 J/cm<sup>2</sup> displays a yellowish brown, clearly visible marking and epoxy resin displays a weak, poorly contrasted engraving. All other plastics could not be marked within the test range. In comparison with other substances which were examined for laser marking with CO<sub>2</sub> lasers, such as Kaolin, Iriodin® pigments could be used with a very low limit value and gave a better contrasted marking. In practice, this means that the laser can be used at a higher pulse frequency thus providing a larger throughput on the production line.

#### Beam deflection method

In the beam deflection method, the laser is directed via two galvanometer mirrors and a lens system to the object to be marked. Using special software, a computer controls the galvanometer mirror. The marking is made by directing the beam in directions x and y. The beam deflection method is very flexible and can transmit a high density of information.

Schematic building of scanner system



The complete contents of the marking with texts, graphics, logos, bar codes, etc., are prepared on the computer. Therefore, there is no need to manufacture and change additional lettering apparatus (masks, punches, engravers, etc.). Beam deflection is not as fast, however, as the mask marking method with a small information content.

The laser types used are:

• Nd:YAG laser with 532 and 1064 nm wavelength

• CW-CO<sub>2</sub> laser (= continuous wave)

In the CW-CO<sub>2</sub> laser, the energy charge is a constant flow and has no energy peaks necessary for carbonisation. The plastic is just melted without leaving an adequately contrasted marking.

• Dot-matrix (CO<sub>2</sub> laser)

The dot matrix method is a special form of the radiation deflection method. Here the beam is only deflected on one plane and the second plane is determined by the speed of the object passing the marking head. This method does not always provide optimum results.



Lasermarked PE plate containing Iridium® LS 850 (Nd: YAG laser)



Lasermarked bottle base with Iridium® LS 800

### Comparison of mask and beam deflection methods

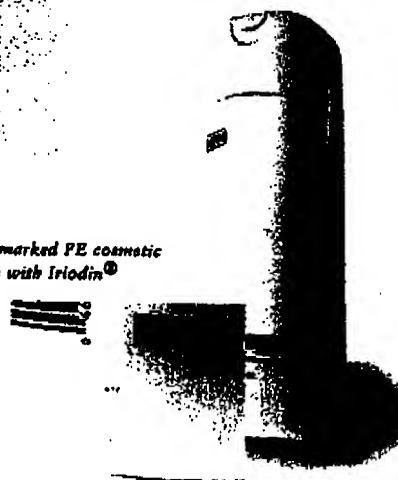
In table 2, the mask and beam deflection methods are compared using typical laser marking systems.

	Maskmarking	Scannermarking
Laser type	CO <sub>2</sub>	Nd:YAG
Inscription size (mm)	10x20	Ø 150 <sup>b</sup>
strength of marking (mm)		
min.	0,05	0,02
max.	10	10
size of characters (mm)		
min.	0,5	0,1
max.	10	100
speed of inscription	up to 50 signs/s	
speed of article marking (m/s)	up to 50	up to 5
cost of investment	+	-
simplicity	+	-
speed of inscription	++	+
inscription size/area		++
quality of inscription		++
flexibility		++

a) Option Ø 120 mm

b) Options Ø 230 mm, 280 mm

Lasermarked PE cosmetic  
bottle with Iridium®



## Merck-the company

Merck operates worldwide. Apart from the German Merck company and Merck AG in Zug, Switzerland, it also includes the Lipha group. We have our own companies in 47 countries and 65 production facilities in 28 countries. Worldwide, more than 25,000 employees work for the group.

The Merck product range includes more than 15,000 different articles in the fields of chemistry, pharmaceuticals, diagnostics as well as technical products.

Merck KGaA is divided into the divisions; Pharmaceuticals, Laboratory, (reagents and diagnostic agents), Fine chemicals, Pigments and Cosmetics.

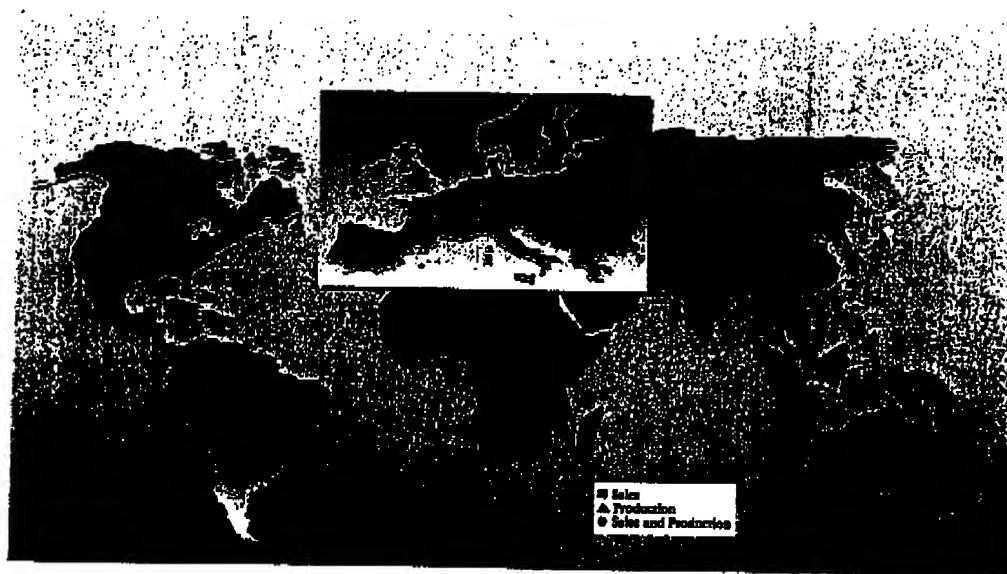
The Pigments and Cosmetics Division supplies products for colour and lustre effects and also many service activities to our customers in the printing-, ceramic-, plastic- and coating industries.

For cosmetic manufacturers, we supply products for decorative cosmetics, sun protection, self-tanning and skin care.

Our research, which is oriented to the needs of our customers, and the environmental compatibility of our products are the most important criteria of success in all business fields.

We advise our customers regarding technical applications to the best of our knowledge within the scope of the possibilities open to us, but without obligation. Current laws and regulations must be observed at all times. This also applies in respect of any protected rights of third parties. Our suggestions do not relieve our customers of the necessity to test our products, on their own responsibility, for suitability for the purpose envisaged. Quotations from our literature are only permitted with our written authority, and the source must be stated.

### Merck-group worldwide



This brochure provides an overview of the application and processing possibilities for Iriodin® and Iriodin® LS for laser marking in different plastics. It provides general information. We shall be pleased to put our decades of experience with Iriodin® pigments at your service if you have more detailed questions. In our laboratories for plastics, equipped with the most modern apparatus, we also investigate individual application problems. Here, we can count on our excellent cooperation with all the world's leading masterbatch and laser manufacturers with whom we jointly search for ways to improve your products.

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